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<p>(21) International Application Number: PCT/GB99/01749 (22) International Filing Date: 2 June 1999 (02.06.99) (30) Priority Data: 9811840.9 2 June 1998 (02.06.98) GB (71) Applicant (for all designated States except US): MATERIALS AND SEPARATIONS TECHNOLOGY INTERNATIONAL LIMITED [GB/GB]; Henley Park, Guildford, Surrey GU13 (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): TENNISON, Stephen, Robert [GB/GB]; 62 Farleigh Road, Addlestone, Surrey KT15 3HR (GB). LEIGH, Benjamin, David [GB/GB]; 10 Avery Court, Alice Road, Aldershot, Hants GU11 HY (GB). (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: CARBON STRUCTURE</p>		
<p>(57) Abstract</p> <p>A stable monolithic porous carbon structure useful for filtration and separation processes can be formed by coating a substrate formed of silica fibres with a resin, curing the resin and carbonising the cured resin, preferably the cured resin is activated by heating in carbon dioxide or steam.</p>		

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Carbon Structure

The present invention relates to a composite structure made from silica and carbon which structure is particularly useful in filtration, separation and adsorption processes.

Carbon in various forms is widely used in separating and filtration processes, for example in removing solids from liquids and from gases, separating liquids from gases, water purification, exhaust gas clean up etc. Carbon is also used as an adsorbent for the adsorption of gases and liquids. Hitherto the carbon has been used as a bed of particulate carbon or as finely divided carbon, for example in the form of charcoal, carbon black etc. The carbon particles can be packed in a bed or bound together with a binder or can be in the form of an activated carbon cloths which has very good adsorption properties but is limited by cost and the fact that is only available as flexible thin sheets.

Solid carbon structures have been made using carbon fibre as in carbon/carbon composites, but these structures do not have any voids in them and are not suitable for separation and filtration processes.

Carbon, because of its chemical and biological inertness, good high temperature properties (particularly in non-oxidising atmospheres) is particularly useful as a filter element or in a separator. However, because of the difficulty of obtaining strong integral carbon structures with the right pore structure, carbon is normally used as an adsorbent in the form of a bed of particles and cannot be used in many applications. There can also be difficulties in the removal of separated material from carbon beds and in the regeneration of the carbon beds.

US Patent 5834114 discloses a method of forming a carbon material for the adsorption of contaminants comprising coating a mineral fibre substrate with a resin,

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cross-linking the resin, heating the coated fibre substrate to carbonise the resin and exposing the coated fibre substrate to an etchant to activate the resin. The only fibres disclosed are glass fibres.

5 As is disclosed in US Patent 5834114, an increase in the activation temperature will produce a surface having a larger pore size than that produced at a lesser activation temperature under the same conditions and this increased pore size enables the structure to be used for a wider range of filtration and separation processes.

10 We have now devised an improved carbon structure and a method of making it, with superior properties.

According to the present invention there is provided a carbon structure which comprises a porous silica substrate having carbon bound to at least the surface of the
15 substrate. The structure has the advantage of being rigid.

The porous silica substrate can be in the form of fibres which are formed into a mat, woven together etc. to form a substrate. The substrate can be in the form of random interlocking fibres which can be self binding to form a mat or batt of the fibres.
20 Suitable silica fibres are made by HITCO Technologies Inc. and are sold under the registered trade mark "Refrasil". The material is sold in the form of mats, bulk fibre, cloth, tape, cordage and yarn. The fibre is refractory and stable up to 980^oC and this enables the resin coated fibre to be heated to this temperature and in the activation stage this can improve the performance and pore characteristics of the carbon
25 structure formed. Glass fibres cannot be effectively heated above 800^oC and this limits the temperature of the processes that can be used for carbonisation and to activate the resin.

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The carbon is preferably in the form of a porous coherent integral layer and is bound directly to the silica substrate without the need for binders etc. The thickness of the carbon layer can be varied according to the need and is preferably up to approximately 10% of the supporting fibre diameter - in the case of the Refrasil fibres
5 this is around 10 microns. The carbon can interpenetrate the fibres and, in the case of mats, the carbon can be in the bulk of the material, i.e. it is not confined to just the outermost surface of the substrate so that a solid three dimensional carbon structure is formed around the silica fibres.

10 By "porous" is meant that the carbon has voids or pores, e.g. it can be a macroporous carbon structure suitable for filtration and separation. The invention provides carbon structures with macropores which are the pores between the coated fibres in the range from 1 to 1000 microns, preferably in the range of 5 to 100 microns.

15 For adsorption processes pore sizes in the range of up to 2 nm (micropores) and from 2 to 30 nm (mesopores) are used. The invention can provide carbon layers on the silica fibres which have pores of these sizes in the carbon layer, which make them useful for adsorption.

20 The structure is monolithic, i.e. it is in a single piece, not granular and not composed of particles bound together by a binder etc; it is in the form of a coherent solid structure.

The invention also provides a method of forming a carbon structure which method
25 comprises contacting a substrate of silica fibres with an uncured resin, curing the resin and carbonising the cured resin.

The resin coats the fibres and, when it is cured it holds or locks the fibres in place. When the resin is carbonised this rigid structure is maintained even though there is a
30 high weight loss on carbonisation. This is very surprising and unforeseen, it being

previously thought the structure would degrade on carbonisation due to the high volumetric shrinkage that usually accompanies the carbonisation of resins.

5 It is thought that the resin, when formed, coats and locks the fibres together to give a rigid macroporous matrix and this is retained on carbonisation.

10 Resins which can be used include phenolic resins which are well known materials and copolymers of phenolic resins with other polymers. Phenolic resins are made by the condensation of a phenol and an aldehyde, e.g. formaldehyde. The condensation
15 is initially carried out to produce a partially condensed product. The condensation may be carried out so as to produce a resin which is fully curable on further heating (Resol). Alternatively, the condensation may be carried out so as to produce a Novolak resin which is only curable when an additional cross-linking agent is mixed with it, e.g. hexamethylene tetramine (known as "hexamine" or "hex"). It is preferred
20 to use Resole resin in the process of the present invention.

EP 0 254 551 gives details of methods of forming porous carbons and the methods and the process steps disclosed for the carbonisation of phenolic resins in this patent
25 can be used in the carbonisation steps in the present invention and its contents are included herein by reference.

Mixed resin systems can also be used such as a phenolic resin as described above mixed with an epoxy resin.

25 It has been surprisingly found that silica fibre forms superior carbon structures compared with glass fibres, the reason for this is not properly understood but is thought to be due to the nature of the bond that is formed between the silica fibre and the resin on carbonisation and is specific for silica fibres.

In one embodiment of the present invention the silica substrate is contacted with the resin forming components e.g. a resole and cured to produce a cured resin according to the known methods. The cured resin is then carbonised to form the carbon structure.

5

The resin forming components can be coated onto the fibres using conventional means. The preferred method comprises dissolving the components in a solvent, coating the silica fibres with the solution and evaporating the solvent off to leave the fibres coated with the resin forming components. Solvents which can be used include
10 alcohols, ketones and proprietary solvents which are commercially available. Solutions of phenolic resin forming components are commercially available and are commonly referred to as resols. The nature and type of solvent will depend on the actual components chosen.

15 The thickness of the resin coating formed on the fibres is affected by the thickness of the fibres, the nature of the resin formed, the concentration of the resin component in the solution, etc. If thicker layers of the resin are required several layers can be sequentially formed by repeated applications and curing to obtain the desired thickness. The thickness of the carbon layer formed will depend on the thickness of
20 the resin layer.

For example, layers of resin of 5 to 20 microns can be formed on silica fibres of 9 microns thickness. This will give a carbon layer thickness on the fibres, after carbonisation of up to about 10 microns. This can be varied as described above.

25

The macropore structure of the final product is influenced by a range of factors such as the thickness, nature and spacing of the silica fibres in the substrate; the closer they are in the starting material the smaller the pore size, thus a woven starting material will give a carbon structure with a different pore size to a needle felt or mat. The
30 silica fibre substrate coated with the resin forming components can be compressed to

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reduce the pore size and the amount, nature and concentration of resin forming components in solution will also influence the pore size in the final material and will enable a material to be made for specific applications.

- 5 The carbonisation steps take place preferably by heating above 600° C for the requisite time, e.g. 11 to 48 hours and takes place under an inert atmosphere or vacuum to prevent oxidation of the carbon.

10 After carbonisation, the porous carbon can optionally be activated to modify the pore volume and surface area. Activation can take place in either steam or carbon dioxide at elevated temperatures above approximately 750° C. The activation process is carried out for a time that varies with the temperature and the activation gas composition and should produce carbon with the requisite properties. Activation can also be carried out in air at temperatures above approximately 300C. This process is
15 highly exothermic and therefore difficult to control and is not normally used in large scale processing. It can however be used advantageously to produce larger micropores than can be produced using steam or carbon dioxide.

20 The shaped carbon materials can be produced by coating a shaped silica substrate with the resin. In this case the silica fibre precursor, such as a woven tube, can be held around a mandrel which is then dipped into the solution of the resin or may be sprayed with a solution of the resin. Alternatively, the precursor can be produced by forming a resin coated silica fibre or cloth known as prepreg around a substrate. These methods are well established and well known to those skilled in the art for the
25 production of fibre reinforced polymer composite materials. A wide variety of forms can be produced using "prepregs" including, for instance, pleated structures, whereby the folded structure is held in place by completing the resin cure during the pleating process. After drying to remove the solvent, the monolith and mandrel are then

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heated to complete the cure at which stage the mandrel can be removed to produce a rigid resin coated silica monolith which can then be carbonised.

5 The silica fibres coated with the resin forming components can be shaped into any desired shape and, on curing, this shape is retained so that after carbonisation a carbon product of the desired shape is formed.

For example, if a tubular shape is required, the coated silica substrate is formed into the tubular shape and on carbonisation a carbon structure of this shape is formed.

10

Surprisingly the carbon structures of the present invention have good structural integrity and rigidity and have no tendency to flake or come away from the silica substrate even under thermal shock and at a temperatures above that which glass fibre based structures can be used. This enables articles to be made from the carbon
15 compositions of the present invention and to form stable three dimensional structures.

20

The carbon structure is porous which enables it to be used in a wide range of filtration and separation processes. The structures have good high temperature properties being stable up to temperatures of around 400 °C and up to 900 °C and higher in non-oxidising atmospheres.

25

They can also be used in the removal of solids from aqueous streams where their chemical and biological inertness makes them particularly suitable for use in cleaning up chemical and process effluent streams. The carbon structures of the present invention can also be used in the removal of particles from organic liquids such as the separation of particles from hydrocarbon fuels, etc. The controlled macro pore size and the ability to form stable three dimensional structures of the carbon compositions of the present invention enables them to be used as absolute filters whilst their structural rigidity enables filtered substances to be more readily removed, e.g. by back
30 flushing, etc. to regenerate the filter.

The high porosity, good mechanical properties and solvent resistance of the carbon structures of the present invention also make them suitable for use as supports for polymeric membranes.

5

The carbon structures are electrically conductive which makes them especially useful where static build up is to be avoided, for example when hydrocarbon liquids such as gasoline and aircraft fuel are to be filtered. The electrical conductivity can also allow the materials to be directly heated by passing an electric current through the structure which can be used to accelerate the desorption of adsorbed materials when the materials are used in adsorbent applications.

10

The controlled micro and meso pore structure of the carbon compositions of the present invention enables them to be used as adsorbents to adsorb vapours and components from liquid streams. The high open macro porosity and the ability to form them into large flat structures makes them particularly suitable for applications where very low pressure drops are required such as in adsorption systems for use in air conditioning and air purification systems in printed circuit manufacturing facilities, vehicle cabin air purification and in the purification of, for instance, water for process use and drinking.

15

20

The materials of the present invention can also be used to combine filtration and adsorption properties into a single element for the purification of both liquid and gaseous streams.

25

The structures can also be used as catalyst support in place of some carbon supports.

The invention is described with reference to the following examples.

Example 1

Mats of silica fibre sold under the Registered Trade Mark Refrasil by HITCO Technologies Inc. which comprised silica fibres of average thickness of
5 approximately 9 microns was contacted with a commercially available resol solution supplied by Blagden Chemicals Ltd. which comprised resinol solids in ethanol. After removing excess resin solution and allowing the impregnated silica mat to partially dry, the material was formed around a plastic mandrel and held in place with wire. The remaining ethanol was then evaporated off and the cure of the resol resin was
10 completed by heating to 150° C in an air oven for one hour. This process was repeated to increase the weight of resin on the silica. At this stage the mandrel was removed, giving a rigid resin impregnated silica tube containing the polymer.

The composition was then placed in a furnace under a gas flow of 8L/min of carbon
15 dioxide and heated to 800° C at 200° C/hour to carbonise the structure, the structure was then oxidised in carbon dioxide at 850° C. After holding at temperature for 30 minutes and cooling back to room temperature, the product was examined and was found to be a solid three dimensional carbon composition which showed no flaking or spalling and was rigid and stable. The carbon content of the carbonised material was
20 determined by placing a small sample of the composite structure in a furnace at 450° C in air and measuring the weight loss. A small sample of the material was also taken and its micropore volume and BET surface area were determined using a Micromeritics ASAP.

25 The results are shown in Table 1 in which 198MAR002 is thin silica paper, 198MAR003 is 1/4 inch unfired random mat and 198MAR004 is 1 inch random fibre mat.

Table 1

Silica form	Sample no	resol solution conc.	no of coats	% weight carbon	oxid time h	% weight loss	%wt carbon after oxidation	BET area m ² /g composite	BET area m ² /g carbon
1/4in batt	1	50/18	1	66.3	2	7	64.6		
	4	50/18	1	65.8	4	22.1	59.6		
	2	50/18	1	66.9	6	27.0	60.0		
	11	50/18	3	76.7	2	5.3	75.7		
	12	50/18	3	72.1	4	17.8	68.1		
	13	50/18	3	75.4	6	24.2	69.9		
	7	50/18	5	77.3	2	5.6	76.3		
	6	50/18	5	77.1	4	15.1	74.0		
	8	50/18	5	79.0	6	24.0	74.1		
	15	50/50	1	50.4	4	26.4	42.8		
	16	50/50	2	60.0	2	8.6	57.8		
	17	50/50	3	70.9	6	26.5	64.2		
	18	50/50	4	72.8	6	26.1	66.4		
198mar002 paper	19	50/50	5	76.2	6	26.3	70.2	658	937.5
	20	50/50	1	55.7	4	32.1	46.1	415.5	901.4
	21	50/50	2	65.9	2	9.9	63.5	367.7	579.3
	22	50/50	3	67.6	6	43.8	54.0	617.0	1142.4
	23	50/50	4	70.8	6	38.5	59.9	658.0	1099.0
	24	50/50	5	72.3	6	38.1	61.7	711.0	1151.5
198mar004 1in fired batt	25	50/50	1	50.6	4	24.6	43.6		
	26	50/50	2	64.9	2	10.6	62.3	310.2	498.0
	27	50/50	3	73.5	6	33.3	64.9		
	28	50/50	4	71.8	6	30.2	63.1		
	29	50/50	5	77.3	6	35.4	68.8	799	1161.9

As can be seen composite media with a surface area of above 800m^2 per gram can be obtained, The material formed is strong and temperature resistance and contains no polymeric material. Filtration tests were carried out on sample 16 and all particles of above 25 microns were rejected in a standard filtration test using an ISO Coarse
 5 A.T.D.12103-1A4 filtration standard.

Example 2

The process of Example 1 was repeated and compared with a glass fibre based
 10 structure made by the same process using a Dow Corning S2 glass fibre using different temperatures for activation.

The results are shown in Table 2 below

Table 2

15

Substrate	Silica Fibre 198 JUN09			Dow Corning S2		
	22			22		
Resin Loading						
Temperature	600 °C	850 °C	900 °C	600 °C	850 °C	900 °C*
Time mins.	30	30	30	30	30	30
20 Carbon Yield	55%	46%	45%	55%	46	
Est. C Content	15.5%	13%	12.7%	15.5%	13	
BET m^2/g	225	46	73	63	17	
Pore vol m^2/g	0.1221	0.026	0.0448	0.0348	0.0113	
Rate min/cc/g C	7.12	7.42	15.36	2.19	24.22	

25

*at 900 °C the results were too low to be measured.

The adsorption kinetics Rate min/cc/g C are derived from the time taken to reach the first data point in the nitrogen adsorption isotherms at a P/Po of 0.0009.

30

It can be seen that the silica based samples, give significantly higher carbon surface areas than the glass (S2) media demonstrating the benefits of the silica materials.

5 The results show that the surface areas and the adsorption kinetics all decline with increasing carbonisation temperature. This decline in performance with heat treatment temperature is even more marked for the Dow S2 glass based material which, whilst it had very good adsorption at 600°C shows a massive deterioration in adsorption kinetics at 850°C This might be attributed to some collapse in the glass fibre at this temperature which is well above the maximum recommended operating
10 temperature (750°C).

In a further set of tests the impacts of resin loading and preparation procedure were examined for several different silica media using the process of example 1 and the results shown in Table 3.

This data encompasses three different silica materials, 3 different resin dilutions (75/25, 50/50 and 50/18), two different resins (Blagden and Hitco) and preparations that include between 1 and 5 resin coats and oxidation for between 2 and 6 hours at 900°C. This data demonstrates that media surface areas of up to 800m²/g are

5 attainable provided that the resin and carbon loadings are optimised with respect to the degree of activation (samples 28 and 29).

Claims

1. A carbon structure which comprises a porous silica substrate having carbon bound to at least the surface of the substrate.
- 5
2. A carbon structure as claimed in claim 1 in which the porous silica substrate is in the form of fibres which are formed into a mat or woven together to form a substrate.
3. A carbon structure as claimed in claim 1 in which the substrate is in the form of random interlocking fibres which is self binding to form a mat or batt of the fibres.
- 10
4. A carbon structure as claimed in any one of claims 1 to 3 in which the carbon is in the form of a porous coherent integral layer and is bound directly to the silica substrate.
- 15
5. A carbon structure as claimed in any one of claims 1 to 4 in which the thickness of the carbon layer is up to 100% of the supporting fibre diameter
6. A carbon structure as claimed in any one of claims 1 to 5 in which the pores between the coated fibres are in the range from 1 to 1000 microns
- 20
7. A carbon structure as claimed in any one of claims 1 to 5 in which the pores between the coated fibres are in the range of 5 to 100 microns.
8. A carbon structure as claimed in any one of claims 1 to 5 in which the pores within the coated fibres are up to 2 nm.
- 25
9. A carbon structure as claimed in any one of claims 1 to 5 in which the pores within the coated fibres are from 2 to 30 nm.
- 30

10. A method for forming a carbon structure which method comprises contacting a substrate of silica fibres with an uncured resin, curing the resin and carbonising the cured resin.
- 5 11. A method as claimed in claim 10 in which the resin is a phenolic resin.
12. A method as claimed in claim 10 or 11 in the silica substrate is contacted with the resin forming components and cured to produce a cured resin and then carbonised to form the carbon structure.
- 10 13. A method as claimed in any one of claims 10 to 13 which comprises dissolving the resin forming components in a solvent, coating the silica substrate with the solution and evaporating the solvent off to leave the fibres coated with the resin forming components.
- 15 14. A method as claimed in any one of claims 10 to 13 in which the carbonisation steps take place by heating above 600°C under an inert atmosphere or vacuum.
- 20 15. A method as claimed in any one of claims 10 to 14 in which, after carbonisation, the porous carbon is activated to modify the pore volume and surface area.
16. A method as claimed in claim 15 in which activation take places by heating in air, steam or carbon dioxide at a temperature of above 750°C . (include air oxidation ?)
- 25 17. A method as claimed in claim 10 to 16 in which the silica substrate, coated with the resin forming components is shaped and, on curing, this shape is retained so that after carbonisation a shaped carbon product is formed.

INTERNATIONAL SEARCH REPORT

International Application No

PC./GB 99/01749

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01D39/20 B01J20/20 B01J20/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 745 416 A (CORNING INC.) 4 December 1996 (1996-12-04) column 6, line 16 -column 8, line 33 column 3, line 15 -column 4, paragraph 1 ---	1,10-17
X	DATABASE WPI Section Ch, Week 8841 Derwent Publications Ltd., London, GB; Class A88, AN 88-288471 XP002115508 & JP 63 209719 A (NIPPON MUKI KK), 31 August 1988 (1988-08-31) abstract --- -/--	1,2,4

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9527 Derwent Publications Ltd., London, GB; Class J01, AN 95-202973 XP002115509 & JP 07 116433 A (MITSUI ENG & SHIPBUILDING CO), 9 May 1995 (1995-05-09) abstract ---	1-4
X	US 4 500 328 A (BRASSELL ETAL.) 19 February 1985 (1985-02-19) column 5, paragraph 2 -column 8, paragraph 1 ---	1,2
A	---	10,11,14
A,P	US 5 834 114 A (ECONOMY ET AL.) 10 November 1998 (1998-11-10) cited in the application the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/01749

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 745416 A	04-12-1996	JP 8332330 A US 5750026 A	17-12-1996 12-05-1998
JP 63209719 A	31-08-1988	JP 2095773 C JP 7114901 B	02-10-1996 13-12-1995
JP 7116433 A	09-05-1995	NONE	
US 4500328 A	19-02-1985	NONE	
US 5834114 A	10-11-1998	AU 5736596 A EP 0831974 A WO 9638232 A	18-12-1996 01-04-1998 05-12-1996